

REMARKS

Claims 1 and 3-9 are pending in the above-identified application.

Claim 2 has been incorporated into claim 1. Claims 3 and 4 have been amended consistent with the changes to pages 6 and 7 of the specification in order to correct minor typographical errors. It is submitted that these minor corrections do not constitute prohibited "new" matter, since a person of ordinary skill in the art would easily and quickly recognize these minor errors, and understand that the named compounds are "(meth)acrylate esters". Please also note that the examples, such as Synthesis Example (1a) at page 13 of the specification, employ the "2-ethyl-2-adamantyl methacrylate" ester which would confirm to a person of ordinary skill in the art the identity of the esters listed in claims 3 and 4 and disclosed at pages 6 and 7 of the specification. Consequently, it is submitted that all of the present claims and the disclosure of the present specification have been properly amended without the introduction of any new matter such that all of the above-noted amendments should be entered of record.

Removal of Claim Objections

Claims 8 and 9 were objected to because of a typographical error. Claims 8 and 9 have been corrected to as to recite the reference to component "(D)" as suggested in the Office Action. Therefore, the basis for these objections has been removed.

Removal of Rejections Under 35 U.S.C. 102(b)

Claims 1, 5 and 8 have been rejected under 35 U.S.C. 102(b) as being anticipated by Padmanaban '690 (USP 5,846,690).

The basis for the above-noted rejection has been removed upon the incorporation of claim 2 (not rejected under 35 U.S.C. 102) into claim 1. Consequently, it is requested that the above-noted rejection be withdrawn.

Issues Under 35 U.S.C. 103(a)

Claims 1-6, 8 and 9 have been rejected under 35 U.S.C. 103(a) as being unpatentable over Barclay '086 (USP 6,492,086) in view of JP '852 (Japanese Patent Application 02-115852 or "Nakamura").

Claims 1-9 have been rejected under 35 U.S.C. 103(a) as being unpatentable over Oomori '704 (Published U.S. Application No. 2002/0034704 A1).

The above-noted rejections are traversed for the following reasons.

Present Invention

The present invention is directed to chemical amplifying positive resist compositions. Upon exposure to light, the acid generator in the compositions of the present invention generates an acid, and the acid catalyzes a cleavage reaction of a protecting group from the resin so that the resin becomes alkali soluble in an exposed resist area.

In summary, JP '852 fails to disclose or suggest any acid generator as required in the present invention; and both of the Barclay '086 and Oomori '704 documents cannot be combined with JP '852 because the components of the compositions of Barclay '086/Oomori '704 serve purposes inconsistent with the components of the composition of JP '852.

Distinctions Between Present Invention and JP '852

An English translations of JP '852 is enclosed. As is apparent from the description of JP '852, specifically the examples therein, the composition disclosed by JP '852 includes an acrylic resin, methyl cellosolve as a solvent, and a plasticizer. JP '852

fails to disclose or suggest the use of any acid generator component as required in the present invention. In fact, the compositions described in JP '852 do not require any acid generator.

Resist patterns using such compositions are formed by a so-called "chain scissioning" mechanism. Upon absorption of deep UV and vacuum UV light, the resist composition undergoes the chain scissioning mechanism, which leads to a reduction of molecular weight of the resin and, as a result, to increased solubility in organic solvents (such as methyl isobutyl ketone, pentoxone, butyl cellosolve, pentoxone, isopropanol and sylene) in the exposed resist area. Consequently, JP '852 fails to disclose or suggest any basis for employing any acid generator which is a significant patentable distinction from the present invention.

Distinctions Between Present Invention and the Barclay '086 and Oomori '704 Documents

Barclay '086 discloses chemically amplified positive-acting resists which include phenolic/alicyclic copolymers. As seen from the description in "BACKGROUND OF THE INVENTION (columns 1 and 2), the description in column 11, lines 29-33, and the description in Example 8 (columns 19 and 20), the compositions disclosed in Barclay

'086 correspond to chemical amplification type resists containing an acid generator.

Oomori '704 disclosed chemical amplification positive-working photoresist compositions which include various specified resinous components, such as components (a1) or (a2) as noted at paragraph [0028]. As seen from the description in "BACKGROUND OF THE INVENTION" ([0001] TO [0004]), the description in "SUMMARY OF THE INVENTION" ([0007] to [0027], the description on [0044] to [0046] and the description in Examples ([0067] to [0086], the compositions disclosed in Oomori '704 correspond to chemical amplification type resists containing an acid generator.

Both Barclay '086 and Oomori '704 fail to disclose or suggest the inclusion of a polyvalent carboxylic acid ester as in component (D) of the composition of the present invention. Therefore, significant patentable distinctions exist between the present invention and the Barclay '086 and Oomori '704 documents.

Inconsistent Features Prevent Attempt to Combine JP '852 with Either
Barclay '086 or Oomori '704

The chain scissioning type resist disclosed by JP '852 operates based on a completely different mechanism than the chemical amplification type resist disclosed by both Barclay '086 and Oomori

'704, such that the components of the compositions in each of these two different types of resists cannot be selectively exchanged as presumed in the Office Action. As background, please see the explanation of these two different types of resists in enclosed Exhibit A: K. Jain, Excimer Laser Lithography, SPIE, Bellingham 1990, p. 135-150. The chain scissioning type resists are referred to in pages 139 to 144 (6.2.3 Chain Scissioning Methacrylate Resist), and the chemical amplification type resists are referred to in pages 144 to 155 (6.2.4 Chemical Amplification Resists). Also attached herewith is Exhibit B: A. Uhl, J. Bendig, J. Leistner, U. Jagdhold, J. Bauer, Proc. SPIE 3333, 1452 (1988) (Proceedings of SPIE, Advances in Resist Technology and Processing XV, Volume 3333, Part Two of Two Parts), which explains behavior of the chain scissioning type resists.

As is evident from the portions noted above in Exhibits A and B, the pattern formation mechanisms and mode of reaction for the chain scissioning type resist and chemical amplification type resist are totally different. Specifically, the chain scissioning type resist requires a "chain scissioning" type mechanism, such as the absorption of UV light, so that the molecular weight of the resin in the composition is reduced in order to increase its solubility in organic solvents (JP '852). On the other hand, chemical

amplification type resists operate by causing a change in the solubility of the resin in alkali by cleavage of a protecting group from the resin by an acid generated from an acid generator (Barclay '086 and Oomori '704). A person of ordinary skill in the art would have no reason to expect that a plasticizer component from a chain scissioning type resist composition as disclosed by JP '852 would provide any satisfactory properties when used in the completely different functioning chemical amplification resist compositions of Barclay '086 or Oomori '704 given the fundamentally different operating mechanisms employed by these two different types of resists as clearly evidenced by the discussion above. Therefore, JP '852 cannot be combined with either Barclay '086 or Oomori '704, such that these rejections must be withdrawn.

Failure of All Documents to Recognize Invention Advantages

In addition to the above, even assuming that prima facie obviousness has been properly alleged, this obviousness is rebutted by the evidence of unexpected advantageous properties provided in the comparative tests results in the present specification. As seen at page 2, lines 4-6, and page 19, lines 7-10 in the present specification, the present composition exhibits higher resolution without impairing resist performance such as application ability and

sensitivity. Please refer to the Examples and Comparative Examples in the present specification. The composition used in Comparative Example 1 is the same composition and is evaluated in the same manner as in Examples 1 to 8 except that it does not contain component (D) a polyvalent carboxylic acid ester. The composition used in Comparative Example 2 is the same composition and is evaluated in the same manner as in Example 9. As is apparent from the Comparative Examples and Examples, effective sensitivity is not enhanced based solely on incorporating the polyvalent carboxylic acid ester (40 mJ/cm² in Comparative Example 1 and 40-44 mJ/cm² in Examples 1-8, 34 μ C in both Comparative Example 2 and Example 9). The compositions in the Examples (present invention) also have higher resolution than Comparative Examples (0.12 μ m in Examples 1-8 and 0.13 μ m in Comparative Example 1, and 0.056 μ m in Example 9 and 0.13 μ m in Comparative Example 2).

JP '852 fails to recognize or suggest any of these advantageous properties. Of course, JP '852 describes a resist composition which operates on a very different mechanism than the resist composition of the present invention. Further, Barclay '086 and Oomori '704 fail to recognize these advantageous properties evidenced by the comparative test results. Consequently, it is submitted that any alleged prima facie obviousness has been rebutted such that the

bases for the above-noted rejections have been removed and these rejections should be withdrawn.

It is submitted for the reasons stated above that the present claims define patentable subject matter such that this application should now be placed condition for allowance.

If any questions arise regarding the above matters, please contact Applicant's representative, Andrew D. Meikle (Reg. No. 32,868), in the Washington Metropolitan Area at the phone number listed below.

Pursuant to the provisions of 37 C.F.R. §§ 1.17 and 1.136(a), the Applicants hereby petition for an extension of three (3) months to February 13, 2004, in which to file a reply to the Office Action. The required fee of \$950.00 is enclosed herewith.

If necessary, the Commissioner is hereby authorized in this, concurrent, and future replies, to charge payment or credit any overpayment to Deposit Account No. 02-2448 for any additional fees

required under 37 C.F.R. §§ 1.16 or 1.17; particularly, extension of
time fees.

Respectfully submitted,

BIRCH, STEWART, KOLASCH & BIRCH, LLP

By



Andrew D. Meikle, #32,868

ADM:gmh
2185-0623P

P.O. Box 747
Falls Church, VA 22040-0747
(703) 205-8000

Attachment(s):

English Translation of JP '852

Exhibit A: K. Jain, Resists for Excimer Laser Lithography, SPIE
Bellingham 1990, pages 135-150;

Exhibit B: A. Uhl, J. Bendig, J. Leistner, U. Jagdhold, J. Bauer,
Proc. SPIE 3333, 1452 (1988) (Proceedings of SPIE, Advances in
Resist Technology and Processing XV, Volume 3333, Part Two of
Two Parts)

Specification

1. Title of the Invention

Method for Manufacturing Semiconductor Device

2. Claims

1. In a method for manufacturing a semiconductor device using a pattern formation process, which comprises forming a thin film of a radio-sensitive positive-type polymer on a substrate; irradiating the thin film with radiation; and developing the thin film, wherein the method for manufacturing a semiconductor device is characterized in that a plasticizer is added to said polymer.

2. The method according to Claim 1, wherein at least one type selected from the group consisting of ditridecyl phthalate, diisodecyl phthalate, di(2-ethylhexyl) adipate, diisodecyl adipate, di(2-ethylhexyl) sebacate and tris(dichloropropyl) phosphate is used as the plasticizer.

3. Detailed Description of the Invention

[Summary]

The invention relates to a method for manufacturing a

semiconductor device using a pattern formation process for a radio-sensitive positive-type resist in order to manufacture a semiconductor integrated circuit.

An object of the invention is to enhance the sensitivity of the resist material so that the throughput is increased.

The method according to the invention is formed by adding a plasticizer to a radio-sensitive positive-type polymer in a pattern formation method, which comprises forming a thin film of the above described polymer on a substrate; irradiating the thin film with radiation; and developing the thin film.

[Field of Industrial Application]

The present invention relates to a method for manufacturing a semiconductor device using a pattern formation process of a radio-sensitive positive-type resist, which is used at the time of manufacture of a semiconductor integrated circuit.

[Prior Art]

In recent years, enhancement of the concentration of elements and increase of the integration have progressed, and at the same time a method for forming a pattern using a high energy radiation such as X-rays or an electron beam, instead of ultra-violet rays that have been conventionally used, has

been developed in a lithographic technology. Poly(methyl methacrylate) (PMMA) is known as a positive-type resist material that can be used in the above described method and is also known as having a high resolution, while having a low sensitivity which requires a long period of time for exposure, and therefore, the throughput becomes low when it is used and the usage thereof is not practical. In addition, materials that include an aromatic ring in a unit structure which is repeated in the material polymer are known as materials having an excellent resistance to dry etching and most of such resist materials have a low sensitivity.

On the other hand, though poly(butene 1-sulfone) (PBS), α -chloro acrylic acid 2, 2, 2-trifluoroethyl and the like are known as highly sensitive resists, they have a poor resolution and the usage thereof is also not practical.

[Problem to be Solved by the Invention]

The above described conventional materials having high resolution, excellent resistance to dry etching and both high resolution and excellent resistance to dry etching all have low sensitivity which is insufficient for a practical use.

The present invention solves the problem of low sensitivity of the resist materials according to the above described prior art and an object of the present invention is to enhance the sensitivity of these materials so that the

throughput in the pattern formation is increased.

[Means for Solving the Problem]

The present invention provides a method for manufacturing a semiconductor device using a pattern formation process, which comprises forming a thin film of a radio-sensitive positive-type polymer on a substrate; irradiating the thin film with radiation; and developing the thin film, wherein the method for manufacturing a semiconductor device is characterized in that a plasticizer is added to said polymer in order to solve the above described problem.

Ditridecyl phthalate (DTDP), diisodecyl phthalate (DIDP), di(2-ethylhexyl) adipate (DOA), diisodecyl adipate (DIDA), di(2-ethylhexyl) sebacate (DOS) and tris (dichloropropyl) phosphate (CRP) can be cited as preferred examples of plasticizers that are useful for the present invention. These plasticizers may be used by themselves, or may be used as a mixture of two or more types.

In the case where the polymer material is an acryl-based polymer such as the above described PMMA, it is preferable for the concentration of the plasticizer to be 3 wt.% to 10 wt.% relative to the weight of the polymer. In addition, in the case where a polymer that includes an aromatic ring in a repeating unit structure is used, it is preferable for the

plasticizer to be of an amount of 3 wt.% to 20 wt.% relative to the weight of the polymer.

[Working Effects]

According to the present invention, it has been found that the unexposed portion of the film is not reduced and the film can be intensified by adding a plasticizer having a concentration in an appropriate range to the resist material.

According to the method of the present invention, the film reduction becomes significant when 10 wt.% or higher of the plasticizer is added in the case where the polymer is an acryl-based polymer. In addition, the concentration of 20 wt.% or higher causes the deterioration of the resolution, while the concentration of 3 wt.% or less leads to the low effects of enhancement of the sensitivity in the case of a polymer that includes an aromatic ring in a repeating unit structure.

[Examples]

The present invention is further explained by citing the following examples.

Comparative Example 1

A methyl cellosolve acetate (MCA) solution of PMMA ($M_w = 300,000$) was applied so that the thickness of the film became 1.1 μm when dried and exposure (20 KeV) to an electron beam

(EB) was carried out on the film after pre-baked for 20 minutes at 170°C. Development was carried out for 2 minutes in methyl isobutyl ketone (MIBK). The sensitivity was 60 $\mu\text{c}/\text{cm}^2$. Line and space (l & s) of 0.375 μm was resolved.

Comparative Example 2

An MCA solution of PMMA ($M_w/600,000$) was applied so that the thickness of the film became 1.0 μm when dried and an EB exposure (20 KeV) was carried out on the film after pre-baked for 20 minutes at 170°C. Development was carried out for 3 minutes in MIBK, and the sensitivity was 40 $\mu\text{c}/\text{cm}^2$. l & s of 0.375 μm was resolved.

Comparative Example 3

An MCA solution of a copolymer ($M_w = 93000$) of α -methyl styrene and methyl α -cyanoacrylate (1:1) was applied so that the thickness of the film became 1 μm when dried, and an EB exposure (20 KeV) was carried out on the film after pre-baked for 20 minutes at 80°C. After that, the film was developed for 3 minutes in pentoxone. The sensitivity was 70 $\mu\text{c}/\text{cm}^2$. l & s of 0.75 μm was resolved.

Comparative Example 4

An MCA solution of a copolymer ($M_w = 32000$) of α -methyl styrene and trifluroethyl α -chloroacrylate (1:1) was applied so that the thickness of the film became 1 μm when dried, and an EB exposure (20 KeV) was carried out on the film after pre-baked for 20 minutes at 170°C. The film was developed

for one minute in butyl cellosolve / isopropanol (IPA) (20:1), and the sensitivity was $25.6 \mu\text{c}/\text{cm}^2$. In addition, 1 & s of $0.375 \mu\text{m}$ was resolved.

Example 1

An MCA solution was made by adding ditiidecyl phthalate (DTDP) of 5 wt.% relative to PMMA ($M_w = 300,000$) to PMMA/MCA. This solution was applied so that the thickness of the film became $1 \mu\text{m}$ when dried and an EB exposure (20 KeV) was carried out on the film after pre-baked for 20 minutes at 170°C . Development was carried out for 2 minutes in MIBK. The sensitivity was $51 \mu\text{c}/\text{cm}^2$. 1 & s of $0.375 \mu\text{m}$ was resolved.

Example 2

The same operation was carried out as in Example 1 except that DTDP of 3 wt.% is added in place of DTDP of 5 wt.% in Example 1. The sensitivity was $58 \mu\text{c}/\text{cm}^2$. In addition, 1 & s of $0.375 \mu\text{m}$ was resolved.

Example 3

An MCA solution was made by adding DTDP of 10 wt.% relative to PMMA ($M_w = 600,000$) to PMMA/MCA. This solution was applied so that the thickness of the film became $1 \mu\text{m}$ when dried and an EB exposure (20 KeV) was carried out on the film after pre-baked for 20 minutes at 170°C . Development was carried out for 3 minutes in MIBK. The sensitivity was $13 \mu\text{c}/\text{cm}^2$. 1 & s of $0.4 \mu\text{m}$ was resolved. In addition, a film reduction of 500\AA occurred.

Example 4

An MCA solution was made by adding DTDP of 3 wt.% relative to a copolymer ($M_w = 93000$) of α -methyl styrene and methyl α -cyanoacrylate (1:1) to copolymer/MCA. This solution was applied so that the thickness of the film became 1 μm when dried, and an EB exposure (20 KeV) was carried out on the film after pre-baked for 20 minutes at 80°C. Development was carried out for 3 minutes in pentoxone. The sensitivity was 68 $\mu\text{c}/\text{cm}^2$. 1 & s of 0.75 μm was resolved.

Example 5

The same operation was carried out as in Example 4 except that diisodecyl adipate (DIDA) of 3 wt.% was added in place of DTDP of 3 wt.% in Example 4. The sensitivity was 64 $\mu\text{c}/\text{cm}^2$ and 1 & s of 0.75 μm was resolved.

Example 6

The same operation was carried out as in Example 4 except that DIDA of 10 wt.% was added in place of DTDP of 3 wt.% in Example 4. The sensitivity was 56 $\mu\text{c}/\text{cm}^2$ and 1 & s of 0.75 μm was resolved.

Example 7

The same operation was carried out as in Example 4 except that DIDA of 20 wt.% was added in place of DTDP of 3 wt.% in Example 4. The sensitivity was 40 $\mu\text{c}/\text{cm}^2$ and 1 & s of 1.0 μm was resolved.

Example 8

An MCA solution was made by adding DTDP of 10 wt.% relative to a copolymer ($M_w = 32000$) of α -methyl styrene and trifluroethyl α -chloroacrylate (1:1) to copolymer/MCA. After a pre-baking of 20 minutes at 170°C and an EB exposure (20 KeV) were carried out on the film, development was carried out for one minute in butyl cellosolve / IPA (20:1). The sensitivity was 18 $\mu\text{c}/\text{cm}^2$ and l & s of 0.375 μm was resolved.

Example 9

The same operation was carried out as in Example 8 except that DTDP of 20 wt.% was added in place of DTDP of 10 wt.% in Example 8. The sensitivity was 16 $\mu\text{c}/\text{cm}^2$ and l & s of 0.4 μm was resolved.

Example 10

The same operation was carried out as in Example 8 except that tris(dichloropropyl) phosphate (CRP) of 20 wt.% was added in place of DTDP of 10 wt.% in Example 8. The sensitivity was 11 $\mu\text{c}/\text{cm}^2$ and l & s of 0.4 μm was resolved.

Comparative Example 5

A monochlorobenzene solution of a copolymer ($M_w = 30000$) of α -methyl styrene and methyl α -chloroacrylate (1:1) was applied so that the thickness of the film became 1.0 μm when dried, and an EB exposure (20 KeV) was carried out on the film after pre-baked for 20 minutes at 180°C. The sensitivity was 17 $\mu\text{c}/\text{cm}^2$ and l & s of 0.3 μm was resolved. Development was carried out for 5 minutes in xylene.

Example 11

A monochlorobenzene solution was made by adding DTDP of 20 wt.% relative to a copolymer ($M_w = 30000$) of α -methyl styrene and methyl α -chloroacrylate (1:1) to copolymer/monochlorobenzene. After a pre-baking of 20 minutes at 180°C and an EB exposure (20 KeV) were carried out on the film, development was carried out for 5 minutes in xylene. The sensitivity was 9 $\mu\text{c}/\text{cm}^2$ and l & s of 0.35 μm was resolved.

Example 12

A monochlorobenzene solution was made by adding DTDP of 10 wt.% to copolymer/monochlorobenzene in place of DTDP of 20 wt.% in Example 11, and after that, the operation was carried out in the same manner as in Example 11 out to form a pattern. The sensitivity was 13 $\mu\text{c}/\text{cm}^2$ and l & s of 0.3 μm was resolved.

Example 13

A monochlorobenzene solution was made by adding di(2-ethylhexyl) sebacate (DOS) of 10 wt.% to copolymer/monochlorobenzene in place of DTDP of 20 wt.% in Example 11, and after that, the operation was carried out in the same manner as in Example 11 to form a pattern. The sensitivity was 11 $\mu\text{c}/\text{cm}^2$ and l & s of 0.3 μm was resolved.

Example 14

A monochlorobenzene solution was made by adding DIDP

of 20 wt.% to copolymer/monochlorobenzene in place of DTDP of 20 wt.% in Example 11, and after that, the operation was carried out in the same manner as in Example 11 to form a pattern. The sensitivity was 11 $\mu\text{C}/\text{cm}^2$ and l & s of 0.35 μm was resolved.

[Effects of the Invention]

As explained above, according to the present invention, an intensifying effect can be given to a resist having a low sensitivity while having both high resolution and excellent resistance to dry etching and thereby the present invention significantly contributes to the practical use of such a resist.

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⑭ 発明の名称 半導体装置の製造方法

⑮ 特 願 昭63-268299

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⑰ 発 明 者 中 村 裕 子 神奈川県川崎市中原区上小田中1015番地 富士通株式会社
内
⑰ 発 明 者 武 智 敏 神奈川県川崎市中原区上小田中1015番地 富士通株式会社
内
⑰ 発 明 者 鶴 永 ゆ かり 神奈川県川崎市中原区上小田中1015番地 富士通株式会社
内
⑱ 出 願 人 富士通株式会社 神奈川県川崎市中原区上小田中1015番地
⑲ 代 理 人 弁理士 青 木 朗 外4名

明 細 書

1. 発明の名称

半導体装置の製造方法

2. 特許請求の範囲

1. 基板上に放射線ポジ型感応性高分子の薄膜を形成し、放射線を照射し、現像することからなるパターン形成工程を用いた半導体装置の製造方法において、上記高分子に可塑剤を添加することを特徴とする半導体装置の製造方法。

2. 可塑剤としてフタル酸ジトリデシル、フタル酸ジイソデシル、アジピン酸ジ-2-エチルヘキシル、アジピン酸ジイソデシル、セバシン酸ジ-2-エチルヘキシル、およびリン酸トリスジクロロプロピルからなる群から選ばれた少なくとも1種が用いられる請求項1記載の方法。

3. 発明の詳細な説明

(概 要)

半導体集積回路の製造のための、放射線感応性ポジ型レジストのパターン形成工程を用いた半導体装置の製造方法に関し、

レジスト材料の感度を上げて、スループットを向上させることを目的とし、

基板上に放射線ポジ型感応性高分子の薄膜を形成し、放射線を照射し、現像することからなるパターン形成方法において、上記高分子に可塑剤を添加することにより構成する。

(産業上の利用分野)

本発明は、半導体集積回路の製造に際して用いる放射線感応性ポジ型レジストのパターン形成工程を用いた半導体装置の製造方法に関する。

(従来の技術)

近年、素子の高密度化および高集積化が進み、これに伴って、リソグラフィ技術においても従来の紫外線に変わって、X線や電子線などの高エネルギー放射線を用いてパターンを形成する方法が開発されている。このような方法に用いることのできるポジ型レジスト材料として知られているポリメタクリル酸メチル(PMMA)は、高解像性である

ことは知られているが、感度が低く、長時間露光を要することとなるため、スループットが低くなり、実用的ではない。また耐ドライエッチング性に優れたものとして、材料高分子の繰り返し単位構造中に芳香族環を含むものが知られているが、該レジスト材料もしばしば低感度となる。

逆に、高感度レジストとして、ポリブテン1-スルホン(PBS)、 α -クロロアクリル酸2,2,2-トリフルオロエチルなどが知られているが、解像性がわるく、これもまた実用的ではない。

〔発明が解決しようとする課題〕

従って、従来においては、高解像性の材料、耐ドライエッチング性に優れた材料および高解像性でかつ耐ドライエッチング性に優れた材料であっても、低感度であるために実用化するのに不充分であった。

本発明は、かかる従来技術におけるレジスト材料の低感度の問題を解決し、これらの材料の感度を上げて、パターン形成におけるスループットを

向上させることを目的とする。

〔課題を解決するための手段〕

本発明は、上記課題を解決するため、基板上に放射線ポジ型感応性高分子の薄膜を形成し、放射線を照射し、現像することからなるパターン形成工程を用いた半導体装置の製造方法において、上記高分子に可塑剤を添加することを特徴とする半導体装置の製造方法を提供する。

本発明に有用な可塑剤の好ましい例としては、フタル酸ジトリデシル(DTDP)、フタル酸ジイソデシル(DIDP)、アジピン酸ジ-2-エチルヘキシル(DOA)、アジピン酸ジイソデシル(DIDA)、セバシン酸ジ-2-エチルヘキシル(DOS)およびリン酸トリシクロロプロピル(CRP)を挙げることができる。これらの可塑剤は単独で用いられてもよく、2種またはそれ以上の混合物として用いられてもよい。

高分子材料が前述したPMMAの如きアクリル系ポリマーである場合、可塑剤濃度はポリマー重量に

対して3~10重量%であるのがよい。また、繰り返し単位構造中に芳香族環を含むポリマーを用いる場合にはポリマー重量の3~20重量%の量で可塑剤を用いるのがよい。

〔作用〕

本発明では、レジスト材料に可塑剤を適当な濃度範囲で添加することによって、未露光部膜減りがなく、増感できることを見出したものである。

本発明の方法において、高分子がアクリル系ポリマーの場合、10重量%以上では膜減りが著しくなる。また、高分子鎖繰り返し単位に芳香環を含むポリマーでは、20重量%以上の濃度では、解像性が劣化し、一方3重量%以下の濃度では、高感度化の効果が小さい。

〔実施例〕

以下に、実施例を挙げて、本発明をさらに説明する。

比較例1

PMMA ($M_w=300,000$)のメチルセロソルブアセート(MCA)の溶液を乾燥厚が1.1 μm になるように塗布し、170℃で20分ブリーク後、電子ビーム(E.B.)露光(20 KeV)を行った。現像はメチルイソブチルケトン(MIBK)中2分にて行った。感度は、60 $\mu c/cm^2$ であった。0.375 μm のラインアンドスペース(L&S)が解像した。

比較例2

PMMA ($M_w/600,000$)のMCA溶液を乾燥厚が1.0 μm になるように塗布し、170℃で20分ブリーク後、E.B.露光(20 KeV)を行った。現像はMIBK中3分にて行い、感度は40 $\mu c/cm^2$ であった。0.375 μm のL&Sが解像した。

比較例3

α -メチルスチレン- α -シアノアクリル酸メチル(1:1)共重合体($M_w=93000$)のMCA溶液を1 μm の乾燥厚で塗布し、80℃で20分ブリーク後、E.B.露光(20 KeV)を行った。その後ペントキソン中3分で現像した。感度は70 $\mu c/cm^2$ で

あった。0.75 μ m の ℓ & s が解像した。

比較例 4

α -メチルスチレン・ α -クロロアクリル酸トリフロロエチル (1 : 1) 共重合体 ($M_w=32000$) の MCA 溶液を 1 μ m の乾燥厚に塗布し、170℃で20分ブリベーク後、E.B.露光(20 KeV)した。現像はブチルセロソルブ/イソプロパノール(IPA) (20 : 1) 中1分で行い、感度は25.6 μ c / cdであった。また、0.375 μ m の ℓ & s が解像した。

実施例 1

PMMA ($M_w=300,000$) に対して5重量%のフタル酸ジトリデシル(DTDP)を加え、MCA溶液とした。乾燥厚1 μ m で塗布し、170℃で20分ブリベーク後、E.B.露光(20 KeV)した。現像は、MIBK中2分で行った。感度は51 μ c / cdとなった。0.375 μ m の ℓ & s が解像した。

実施例 2

実施例 1 の5重量%のDTDPに代え、3重量%のDTDPを加え、同様な実験を行った。感度は58 μ c / cdであった。また、0.375 μ m の ℓ & s が解像し

0.75 μ m の ℓ & s が解像した。

実施例 6

実施例 4 の3重量%のDTDPに代え、10重量%のDIDAを加え、実施例 4 と同様な実験を行った。感度は56 μ c / cdであり、0.75 μ m の ℓ & s が解像した。

実施例 7

実施例 4 の3重量%のDTDPに代え、20重量%のDIDAを加え、実施例 4 と同様な実験を行った。感度は40 μ c / cdであり、1.0 μ m の ℓ & s が解像した。

実施例 8

α -メチルスチレン・ α -クロロアクリル酸トリフロロエチル (1 : 1) 共重合体 ($M_w=32000$) に対し、10重量%のDTDPを加え、MCA溶液とした。170℃で20分ブリベークし、E.B.露光(20 KeV)後、現像をブチルセロソルブ/IPA (20 : 1) 中1分で行った。感度は18 μ c / cdであり、0.375 μ m の ℓ & s が解像した。

た。

実施例 3

PMMA ($M_w=600,000$) に対して10重量%のDTDPを加え、MCA溶液とした。1 μ m の乾燥厚に塗布し、170℃で20分ブリベーク後、E.B.露光(20 KeV)した。現像はMIBK中3分で行った。感度は13 μ c / cdであった。0.4 μ m の ℓ & s が解像した。また、500Åの膜減りが生じた。

実施例 4

α -メチルスチレン・ α -シアノアクリル酸メチル (1 : 1) 共重合体 ($M_w=93000$) に対して3重量%のDTDPを加え、MCA溶液とした。1 μ m の乾燥厚に塗布後、80℃で20分ブリベークし、E.B.露光(20 KeV)を行った。現像はペントキソン中3分で行った。感度は68 μ c / cdであり、0.75 μ m の ℓ & s が解像した。

実施例 5

実施例 4 の3重量%のDTDPに代え、3重量%のアジピン酸ジイソデシル(DIDA)を加え、実施例 4 と同様な実験を行った。感度は64 μ c / cdであり、

実施例 9

実施例 8 の10重量%のDTDPに代え、20重量%のDTDPを加えた。以下、実施例 8 と同様な実験を行った。感度は16 μ c / cdであり0.4 μ m の ℓ & s が解像した。

実施例 10

実施例 8 の10重量%のDTDPに代え、20重量%のリン酸トリスジクロロプロピル(CRP)を加えた。以下実施例 8 と同様な実験を行った。感度は11 μ c / cdであり、0.4 μ m の ℓ & s が解像した。

比較例 5

α -メチルスチレン・ α -クロロアクリル酸メチル (1 : 1) 共重合体 ($M_w=30000$) のモノクロルベンゼン溶液を乾燥厚1.0 μ m で塗布し、180℃で20分ブリベークした後、E.B.露光(20 KeV)した。感度は17 μ c / cdであり、0.3 μ m ℓ & s が解像した。現像はキシレン5分で行った。

実施例 11

α -メチルスチレン・ α -クロロアクリル酸メチル (1 : 1) 共重合体 ($M_w=30000$) に対し、

20重量%のDTDPを加え、モノクロルベンゼン溶液とした。180℃で20分ブリベークし、E.B.露光(20 KeV)後、キシレン中5分で現像した。感度は9 $\mu\text{c}/\text{cm}^2$ であり、0.35 μm の ℓ & s が解像した。

実施例12

実施例11の20重量%のDTDPに代え、10重量%のDTDPを加え、モノクロルベンゼン溶液とし、以下実施例11と同様な操作でパターンニングを行った。感度は13 $\mu\text{c}/\text{cm}^2$ であり、0.3 μm の ℓ & s が解像した。

実施例13

実施例11の20重量%のDTDPに代え、10重量%のセバシン酸ジ-2-エチルヘキシル(DOS)を加えてモノクロルベンゼン溶液とし、以下実施例11と同様な操作でパターンニングを行った。感度は11 $\mu\text{c}/\text{cm}^2$ であり、0.3 μm の ℓ & s が解像した。

実施例14

実施例11の20重量%DTDPに代え、20重量%DTDPを加え、モノクロルベンゼン溶液として、

以下実施例11と同様な操作でパターンニングを行った。感度は11 $\mu\text{c}/\text{cm}^2$ であり、0.35 μm の ℓ & s が解像した。

(発明の効果)

以上説明したように、本発明によれば、高解像性かつ耐ドライエッチング性に優れたレジストでありながら、低感度であるレジストに対して増感効果を与えることができ、実用化に寄与するところが大きい。

特許出願人

富士通株式会社

特許出願代理人

弁理士	青	木	朗
弁理士	内	田	幸男
弁理士	石	田	敬
弁理士	山	口	昭之
弁理士	西	山	雅也